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(71)出願人 899000046

関西ティ-エル-オー株式会社

京都府京都市下京区中堂寺栗田町93番地

(72)発明者 長谷川 靖哉

大阪府豊中市柴原町3-2-22-102

(72)発明者 柳田 祥三

兵庫県川西市鶯台2-10-13

(72)発明者 和田 雄二

大阪府豊中市西緑丘2-2-6-643

(74)代理人 100095670

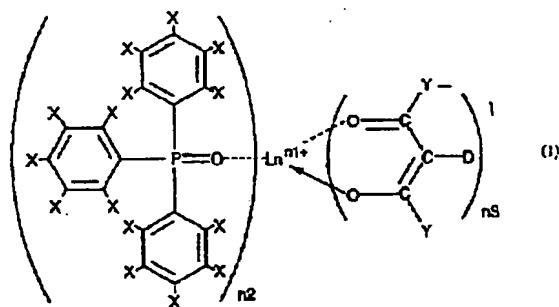
弁理士 小林 良平 (外1名)

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(54)【発明の名称】 希土類錯体並びにそれを用いた光機能材料及び発光装置

(57)【要約】 (修正有)

【解決手段】一般式 (I) [式中、Lnは希土類原子を、n1は2または3を、n2は1または2を、n3は1、2、3または4を示す。Xは水素原子、重水素原子、ハロゲン原子 (F, Cl, Br, I)、C<sub>1</sub>~C<sub>20</sub>の基、水酸基、ニトロ基、アミノ基、スルホニル基、シアノ基、シリル基、ホスホン酸基、ジアゾ基、メルカプト基を示す。YはC<sub>1</sub>~C<sub>20</sub>の基、水酸基、ニトロ基、アミノ基、スルホニル基シアノ基、シリル基、ホスホン酸基、ジアゾ基、メルカプト基を示す。Dは重水素原子を示す。] で表される、光機能材料用の希土類錯体。それを透明固体担体に含ませた光機能材料。それとLEDまたは半導体レーザーとの組み合わせによる発光装置。



【効果】本発明の希土類錯体およびそれを含む透明固体担体は光の変換効率が高く、LEDまたは半導体レーザーとの組み合わせにより新規な発光装置として有用であり、一般照明装置、信号装置、表示装置などへの応用が可能である。

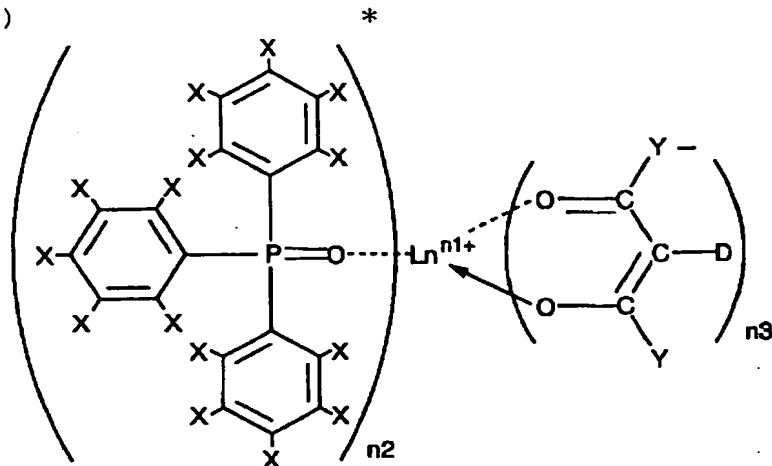
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【特許請求の範囲】

【請求項1】 一般式(I)

\* 【化1】



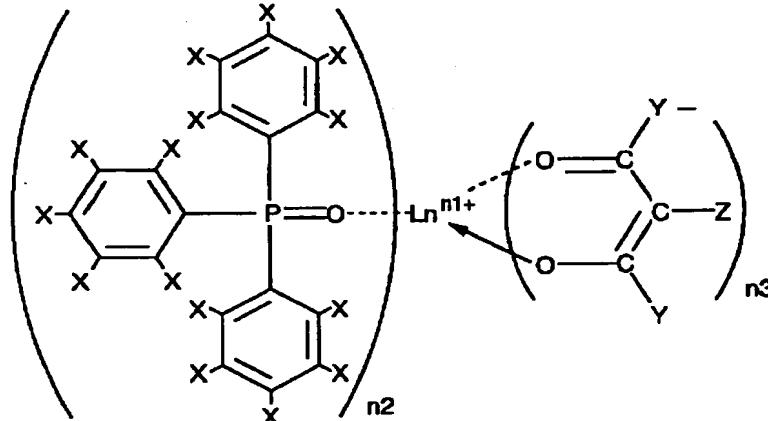
【式中、Lnは希土類原子を示し、n1は2または3を示す。n2は1または2を示す。n3は1、2、3または4を示す。Xは同一または異なる水素原子、重水素原子、ハロゲン原子、C<sub>1</sub>~C<sub>20</sub>の基、水酸基、ニトロ基、アミノ基、スルホニル基、シアノ基、シリル基、ホスホン酸基、ジアゾ基、メルカプト基を示す。Yは同一または異なるC<sub>1</sub>~C<sub>20</sub>の基、水酸基、ニトロ基、アミノ基、スル

※ホニル基シアノ基、シリル基、ホスホン酸基、ジアゾ基、メルカプト基を示す。Dは重水素原子を示す。】で表される、光機能材料用の希土類錯体。

【請求項2】 請求項1記載の希土類錯体を含む光機能材料用透明固定担体。

【請求項3】 一般式(II)

【化2】



【式中、Ln、n1、n2、n3、X、Yは上記と同じであり、Zは水素原子または重水素原子を示す。】で表される希土類錯体の結晶または該希土類錯体を含む透明固定担体と、該錯体の中心イオンLn<sup>n1+</sup>のf-f遷移または該錯体の配位子の吸収に対応する励起光を発する発光ダイオードまたは半導体レーザーとを組み合わせることを特徴とする発光装置。

【請求項4】 上記中心イオンLn<sup>n1+</sup>がEu<sup>3+</sup>であることを特徴とする請求項3に記載の発光装置。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、有用な光学特性を備えた希土類錯体、並びにそれを応用した光機能材料及び発光装置に関する。

【0002】

【従来の技術】電子材料の開発は目覚ましく、オプトエレクトロニクス分野で光機能材料の開発が多数行われ

ている。例えば、レーザー光線用電子デバイスとして、ネオジムを含むガラスが実用化されている。しかし、その製造及び加工が難しく、製造費が高いため、用途が限られている。

【0003】特開昭64-26583号には、発光性を有するポリマー組成物として、チオフエンおよびCF<sub>3</sub>を置換基として有するβ-ジケトン/Eu錯体のアンモニウム塩を含有する樹脂組成物が開示されている。さらに、特願平10-238973には、発光性を有するポリマー組成物として、CF<sub>3</sub>を置換基として有する重水素化β-ジケトン/Eu錯体またはスルホネート/Eu錯体を含有する樹脂組成物が開示されている。

【0004】

【発明が解決しようとする課題】しかしながら、これら樹脂組成物は発光特性が未だ満足できるレベルに達していなかった。

【0005】それに対し、本件発明者の一部はエネルギー

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ーギャップ理論の再検討から始めることにより、1995年に世界で初めて、有機媒体中で発光可能なネオジウム等の希土類金属の一群の錯体の設計に成功した(長谷川靖哉、「有機媒体中で光らないネオジウムをどのように光らせるか?」、化学と工業、第53巻(2000)第2号、pp.126-130)。これらの一部については特許出願も行った(PC T/JP98/00970=W098/40388公報、特願平10-238973=特開2000-63682公報、特願平11-62298=特開2000-256251公報)。

【0006】これら錯体は、350℃という高温においても安定であり光劣化が生じにくく、有機化合物は熱や光照射によって劣化が生じやすいという従来の常識を覆すものである。また、プラスチックやポリマーという樹脂系のホスト材料との親和性も高く、容易な加工性と相まって次世代の光素子となることが期待されている。

【0007】そこで、本願発明者らは、これらの優れた発光特性を有する組成物、およびそれらとLEDまたは半導体レーザーとを組み合わせさせた発光装置の特許出願した(特願2001-135116号)

【0008】本発明者らは、錯体に関して更に研究を続ける中で、吸光・発光特性がさらに優れた組成物を見いだすに至り、今般、その組成物自体、およびそれを用いた光機能材料、更には、それとLEDまたは半導体レーザーとの組み合わせによる発光装置を提供するものである。

【0009】

【課題を解決するための手段】本発明に係る組成物は、図1の一般式(II)で表される希土類錯体である。

【0010】図1の一般式(II)において、Lnは希土類原子を示し、n1は2または3を示す。n2は1または2を示す。n3は1、2、3または4を示す。Xは同一または異なる水素原子、重水素原子、ハロゲン原子(F, Cl, Br, I)、C<sub>1</sub>~C<sub>20</sub>の基、水酸基、ニトロ基、アミノ基、スルホニル基、シアノ基、シリル基、ホスホン酸基、ジアゾ基、メルカプト基を示す。Yは同一または異なるC<sub>1</sub>~C<sub>20</sub>の基、水酸基、ニトロ基、アミノ基、スルホニル基、シアノ基、シリル基、ホスホン酸基、ジアゾ基、メルカプト基を示す。Zは水素原子または重水素原子を示す。

【0011】

【発明の実施の形態】各構成要素について、更に詳細に説明する。

【0012】C<sub>1</sub>~C<sub>20</sub>の基としては；

\* 直鎖又は分枝を有するアルキル基(C<sub>n</sub>H<sub>2n+1</sub>；n=1~20)、およびパーフルオロアルキル基(C<sub>n</sub>F<sub>2n+1</sub>；n=1~20)、パークロロアルキル基(C<sub>n</sub>Cl<sub>2n+1</sub>；n=1~20)などの直鎖又は分枝を有するパーハロゲン化アルキル基；

【0013】\* 直鎖又は分枝を有するアルケニル基(ビニル基、アリル基、ブテニル基)、およびパーフルオロアルケニル基(パーフルオロビニル基、パーフルオ

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ロアリル基、パーフルオロブテニル基)、パークロロアルケニル基などの直鎖又は分枝を有するパーハロゲン化アルケニル基；シクロアルキル基(C<sub>n</sub>H<sub>2n-1</sub>；n=3~20)、およびパーフルオロシクロアルキル基(C<sub>n</sub>F<sub>2n-1</sub>；n=3~20)、パークロロアルキル基(C<sub>n</sub>Cl<sub>2n-1</sub>；n=3~20)などの直鎖又は分枝を有するパーハロゲン化アルキル基；シクロアルケニル基(シクロペンチル基、シクロヘキシル基等)、およびパーフルオロシクロアルケニル基、パークロロアルケニル基などのパーハロゲン化アルキル基；

【0014】\* フェニル基、ナフチル基、ビフェニル基等の芳香族基、およびパーフルオロフェニル基、パーフルオロナフチル基、パーフルオロビフェニル基、パークロロフェニル基、パークロロナフチル基、パークロロビフェニル基などのパーハロゲン化芳香族基；

【0015】\* ピリジル基等のヘテロ芳香族基、およびパーフルオロピリジル基等のパーハロゲン化ヘテロ芳香族基；

【0016】\* ベンジル基、フェネチル基等のアラルキル基、およびパーフルオロベンジル基などのパーハロゲン化アラルキル基；

【0017】等を挙げることができる。

【0018】XおよびYで示されるC<sub>1</sub>~C<sub>20</sub>の基には、必要に応じて重水素原子、ハロゲン原子(F, Cl, Br, I)、水酸基、ニトロ基、アミノ基、スルホニル基、シアノ基、シリル基、ホスホン酸基、ジアゾ基、メルカプト基などの置換基で置換されていていてもよい。

【0019】また、C<sub>1</sub>~C<sub>20</sub>の基の任意の位置のC-C単結合の間に-O-、-COO-、-CO-を一個または複数個介在させて、エーテル、エステル、ケトン構造としてもよい。

【0020】XおよびYがアルケニル基である一般式(II)の希土類錯体を、必要に応じてエチレン、プロピレンなどのオレフィンおよびハロゲン化オレフィン重合させて高分子希土類錯体としてもよい。

【0021】一般式(II)で表される化合物において、Yとしては、前記のものが使用可能であるが、特に、希土類錯体あるいは希土類錯体を含む透明固体担体の安定性および発光強度の点を考慮すると、炭素数1~4のアルキル基、パーハロゲン化アルキル基、芳香族基、パーハロゲン化芳香族基、ヘテロ芳香族基、パーハロゲン化ヘテロ芳香族基が好ましく、なかでもパーフルオロアルキル基、芳香族基、ヘテロ芳香族基が最も好ましい。

【0022】Lnで表される希土類元素としては、La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Luなどのランタン系列元素が挙げられ、好ましくはNd, Eu, Tb, Ybが挙げられる。

【0023】n1は2または3であるが、好ましくは3を示す。n2は1または2であるが、好ましくは2を示す。n3は1~4のいずれかであるが、好ましくは3を示す。

【0024】一般式(II)で表される錯体と重水素化剤を

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重水素置換反応することにより、請求項1に記載した一般式(I)の錯体(Zが重水素原子Dであるもの)が得られる。用いられる重水素化剤は、重水素を含むプロトン性化合物、具体的には、重水、重水素化メタノール、重水素化エタノールなどの重水素化アルコール、重塩化水素、重水素化アルカリなどが挙げられる。反応を促進させるためにトリメチルアミン、トリエチルアミンなどの塩基剤や添加剤を加えてもよい。重水素置換反応は一般式(II)で表される錯体と重水素化剤を混合することにより得られるが、反応時に非プロトン性の溶媒を加えてもよい。非プロトン性溶媒としてはアセトン、メチルエチルケトン等のケトン系溶媒、ジエチルエーテル、テトラヒドロフラン等のエーテル系溶媒、クロロホルム、塩化メチレン等のハロゲン系溶媒、DMSO、DMF等が挙げられる。中でも一般式(II)が溶解可溶性溶媒が好ましい。

【0025】また、用いる重水素化剤の量としては、一般式(II)で表される錯体の総量(1重量部とする)に対して1~100重量部程度が例示され、好ましくは1~20重量部程度である。

【0026】混合する方法としては特に限定されず、室温から150℃の温度で、好ましくは30℃から100℃の温度で、必要に応じて攪拌下、0.1~100時間、好ましくは0.1~20時間混合すればよい。

【0027】攪拌後、重水素化剤および溶媒を留去することにより、一般式(I)で表される錯体を得られる。また、必要に応じて、再結晶、カラムクロマト、昇華等の方法によりさらに精製可能である。

【0028】上記の方法により一般式(I)および一般式(II)で表される希土類錯体が調製できる。

【0029】本発明に係る希土類錯体の吸光・発光特性については、後に詳しく述べる。

【0030】上記有用な吸光・発光特性を有する希土類錯体を透明固体担体に含有させることにより、発光補助体、光学レンズ等の種々の光機能材料に用いることができる。なお、上記希土類錯体の結晶自体も、もちろん同様に光機能材料として用いることができる。

【0031】更に、これら希土類錯体の結晶または希土類錯体を含む透明固体担体と、その希土類錯体の中心イオンのf-f遷移または配位子の吸収に対応する励起光を発する発光ダイオードまたは半導体レーザーとを組み合わせた発光装置は、発光効率の高い発光装置として使用することが可能である。

【0032】上記の透明固体担体としては、透明ポリマーマトリックスや透明ガラス等を使用することができる。

【0033】透明ポリマーマトリックスとしては、ポリメチルメタクリレート、含フッ素ポリメタクリレート、ポリアクリレート、含フッ素ポリアクリレート、ポリスチレン、ポリエチレン、ポリプロピレン、ポリブテン等のポリオレフィン、含フッ素ポリオレフィン、ポリビニル

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エーテル、含フッ素ポリビニルエーテル、ポリ酢酸ビニル、ポリ塩化ビニル、及びそれらの共重合体、セルロース、ポリアセタール、ポリエステル、ポリカーボネイト、エポキシ樹脂、ポリアミド樹脂、ポリイミド樹脂、ポリウレタン、ナフィオン、石油樹脂、ロジン、ケイ素樹脂などが例示され、好ましくはポリメチルメタクリレート、含フッ素ポリメタクリレート、ポリアクリレート、含フッ素ポリアクリレート、ポリスチレン、ポリオレフィン、ポリビニルエーテル、及びそれらの共重合体、エポキシ樹脂等を使用することができる。もちろん、これらの2種以上を組み合わせたものであってもよい。

【0034】透明ポリマーマトリックスや透明ガラス等に希土類錯体を含有させる場合、その透明性を高めるために、同時に極性溶媒を含ませることもできる。

【0035】極性溶媒としては、例えばDMSO-d<sub>6</sub>(ジメチルスルホキシド)を用いることができる。

【0036】

【発明の効果】本発明の希土類錯体およびそれを含む透明固体担体は光の変換効率が高く、LEDまたは半導体レーザーとの組み合わせにより新規な発光装置として有用であり、一般照明装置、信号装置、表示装置などへの応用が可能である。

【0037】本発明の希土類錯体は、配位子の構造及び/又は希土類原子の種類を変更することにより、発光波長を変化させることができ、任意の波長の発色を得ることができる。

【0038】

【実施例】以下、本発明を実施例に基づき、より詳細に説明するが、本発明自体はこれら実施例により限定されないことはもちろんである。

【0039】Eu(hfa-H)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>錯体の合成

酢酸ユウロピウム(Eu(CH<sub>3</sub>COO)<sub>3</sub>: 5g, 12.5mmol)を50mlの蒸留水へ溶かし、ヘキサフルオロアセチルアセトン(hfa)(CF<sub>3</sub>COCH<sub>2</sub>COCF<sub>3</sub>: 7g, 33.6mmol)を加え、室温で3時間攪拌した。沈澱した固体を濾過、水洗後、メタノールと蒸留水で再結晶を行って目的の錯体(Eu(hfa-H)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>: 淡黄色)を得た。得られた錯体は示差熱分析(DSC)により、2水和物であることを確認した。IR(c m<sup>-1</sup>): 3450(O-H st.), 1650(C=O st.), 1250~1150(C-F) 19F-NMR(アセトン-d<sub>6</sub>, 標準物質C<sub>6</sub>F<sub>6</sub>: ppm): -78.3(CF<sub>3</sub>)

【0040】Eu(hfa-H)<sub>3</sub>(TPPO)<sub>2</sub>錯体の合成

実施例1で得られた錯体(Eu(hfa-H)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> 5.77g)とトリフェニルホスフィンオキサイド(TPPO: 2.97g)を100mlのメタノールに溶かし、12時間加熱還流を行った。12時間後、メタノールを減圧留去により取り除き、白色生成物を得た。この粉体をトルエンで洗浄し、未反応のEu(hfa-H)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>錯体を吸引ろ過により取り除いた後、トルエンを減圧留去した。得られた生成物をヘキサンで

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洗浄し、粉体を得た。収量は5.28g、収率は74%であった。トルエン、ヘキサン混合溶媒により再結晶を行うことにより、目的の錯体  $(\text{Eu}(\text{hfa-H})_3(\text{TPPO})_2)$  を得た。

IR( $\text{cm}^{-1}$ ): 1650(C=O), 1250~1150(C-F), 1125(P=O)

$^{19}\text{F}$ -NMR (アセトン- $\text{d}_6$ , 標準物質  $\text{C}_6\text{F}_6$ ; ppm):  $\delta$ -76.7 (s, C-F)

$^1\text{H}$ -NMR (アセトン- $\text{d}_6$ , 標準物質 TMS; ppm):  $\delta$  7.6 (m, aromatic C-H), 5.4 (s, C-H) 元素分析 ( $\text{EuC}_{51}\text{H}_{33}\text{O}_8\text{F}_{18}\text{P}_2$ )

実測値 C, 45.94; H, 2.57%

計算値 C, 45.96; H, 2.50%

#### 【0041】 $\text{Eu}(\text{hfa-D})_3(\text{TPPO})_2$ の合成

実施例2で得られた錯体の重水素化反応は、公知の文献 (Hasegawa, Y.; Murakoshi, K.; Wada, Y.; Yanagida, S.; Kim, J.; Nakashima, N.; Yamanaka, T. J. Phys. Chem. 1996, 100, 10201.) に従った。得られた粉体を十分に乾燥し、目的の錯体  $(\text{Eu}(\text{hfa-D})_3(\text{TPPO})_2)$  を得た。

#### 【0042】 $\text{Eu}(\text{hfa-D})_3(\text{TPPO})_2$ を含むポリマーの作成

実施例3で得られた錯体を含むポリマーは、公知の文献 (Hasegawa, Y.; Sogabe, K.; Wada, Y.; Kitamura, T.; Nakashima, N.; Yanagida, S. Chem. Lett. 1999, 35.) に従い調製を行った。

#### 【0043】 発光特性

$\text{Eu}(\text{hfa-D})_3(\text{TPPO})_2$  を含むPMMAポリマー (A, B) の発光特性を図2に示す。比較として、文献記載の希土類錯体を含むPMMAポリマー (Hasegawa, Y.; Sogabe, K.; Wada, Y.; Kitamura, T.; Nakashima, N.; Yanagida, S. Chem. Lett. 1999, 35.) (C, D) の発光特性を同じグラフに示す。図2より、本発明の錯体を含む透明固体担体 (A, B) は、文献記載のもの ( $\text{Eu}(\text{hfa-D})_3(\text{D}_2\text{O})_2$  を含むPMMA) (C, D) に比べて発光量子収率が飛躍的に向上していることがわかる。

【0044】 図3に、各サンプルの発光スペクトルのグラフを示す。縦軸のスペクトル強度は、590nmの発光強度を1として規格化した。励起波長は、錯体の中心イオンである  $\text{Eu}^{3+}$  のf-f遷移に対応する465nmである。本発明の実施例であるサンプルA ( $\text{Eu}(\text{hfa-D})_3(\text{TPPO})_2$  を含むPMMA) は、615nm (赤色) の発光強度が相対的に強くなっていることがわかる。また、図3において注目されるのは、各サンプルのピーク強度比が異なることである。これは、配位子の選択及び添加剤の有無 (多寡) を適宜設計することにより、発光の演色性を或る範囲で調整することができることを示している。

【0045】 図4に本発明の実施例であるサンプルA ( $\text{Eu}(\text{hfa-D})_3(\text{TPPO})_2$  を含むPMMA) の励起スペクトルを示す。465nmの鋭いピークその他、370~450nmにブロードな吸収帯を持っている。465nmは上記の通り中心イオン  $\text{Eu}^{3+}$  のf-f遷移によるものであり、370~450nmのブロード

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な吸収帯は多くのf-f遷移が重なり合ったもの、または配位子によるものと思われる。

【0046】 図5は、InGaN青色LEDの上にサンプルA ( $\text{Eu}(\text{hfa-D})_3(\text{TPPO})_2$  を含むPMMA) をかぶせ、その透過光のスペクトルを測定したものである。InGaN-LEDは、その発光波長の中心が465nmとなるようにその成分変数xを調整したものであり、450~500nmの範囲で発光ピークを有するが、その中で465nmにおいて希土類錯体  $\text{Eu}(\text{hfa-D})_3(\text{TPPO})_2$  の中心イオン  $\text{Eu}^{3+}$  のf-f遷移による急峻な吸収ピークが生じている。また、615nmに大きな発光ピークが現れており、591nm付近及び700nm付近においても小さな発光ピークが現れている。図2に示した通り、これらは約70%という高い発光効率を得られている。

【0047】 図6は、サンプルA ( $\text{Eu}(\text{hfa-D})_3(\text{TPPO})_2$  を含むPMMA) の370~450nmのブロードな励起光範囲に入るようにInGaN-LEDの成分変数xを調整し、発光波長を405nmとして同様の測定を行った結果である。この場合も同様に、615nm付近に大きなピークが現れ、591nmと700nm付近に小さなピークが現れている。

【0048】 図7は、従来の白色LED (InGaN青色LEDをYAG蛍光体で覆ったもの) の上にサンプルA ( $\text{Eu}(\text{hfa-D})_3(\text{TPPO})_2$  を含むPMMA) をかぶせて同様の測定を行った結果である。465nmにおいて  $\text{Eu}^{3+}$  のf-f遷移による吸収ピークが明瞭に認められる。そして、その結果として、615nm付近に大きな発光ピークが現れている。この図から明らかのように、このようにして作製される発光装置は、従来の白色LEDにおいて欠けていた赤色成分を補った理想的な白色に近いものとなり、それを用いた光源は非常に演色性の高い白色光源となる。これは、手術や商品ディスプレイ等、色識別力或いは演色性が特に必要とされる分野において有用な光源として利用することができる。

【0049】 本発明に係る希土類錯体はこのような吸光特性を有するため、LEDまたは半導体レーザーをその励起光源として組み合わせることにより、高効率な波長変換光機能材料として有用に利用することができる。特に、図4に示されるような370~450nmのブロードな吸収帯は、例えばEL等の広帯域発光体との組み合わせに大きな効果をもたらすものと考えられる。

【0050】 このような波長変換光機能材料、及びそれとLEDまたは半導体レーザーとの組み合わせによる発光装置の有用性については、上記の先の出願 (特願2001-135116) において詳細に論じている。本発明に係る希土類錯体及びそれを含む透明固体担体である光機能材料、更にはそれとLED、半導体レーザー及びその他の発光体との組み合わせによる発光装置は、同様の産業的有用性を社会に提供するものである。

#### 【図面の簡単な説明】

【図1】 本発明に係る希土類錯体の一般式。

【図2】 本発明の実施例である希土類錯体と比較化合

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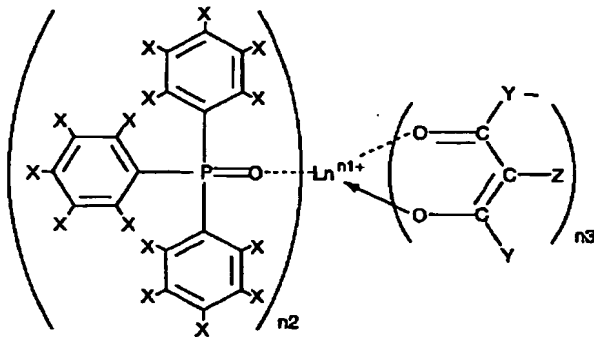
物の希土類錯体の発光特性の対比表。

【図3】 本発明の実施例である希土類錯体と比較化合物の希土類錯体の発光スペクトルのグラフ。

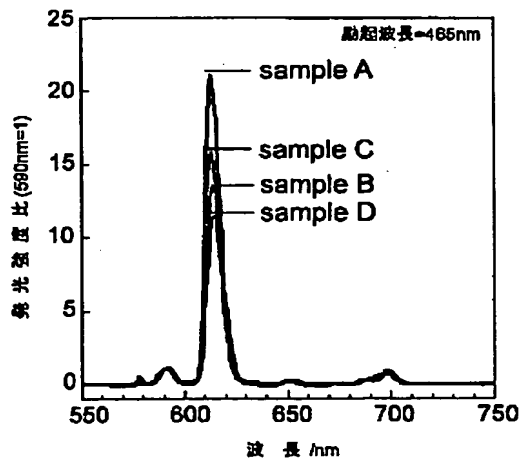
【図4】 本発明の実施例である希土類錯体の励起スペクトルのグラフ。

【図5】 中心発光波長465nmのInGaN青色LED上にサンプルAをかぶせ、その透過光のスペクトルを測定した結果のグラフ。

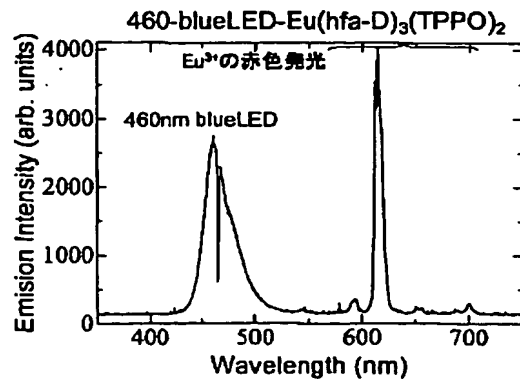
【図1】



【図3】



【図5】



(6)

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果のグラフ。

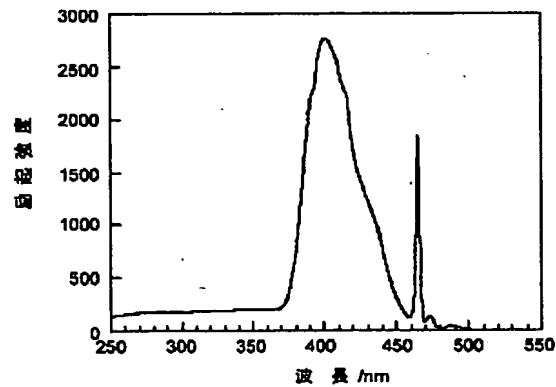
【図6】 中心発光波長405nmのInGaN紫色LED上にサンプルAをかぶせ、その透過光のスペクトルを測定した結果のグラフ。

【図7】 InGaN青色LEDをYAG蛍光体で覆った白色LED上にサンプルAをかぶせ、その透過光のスペクトルを測定した結果のグラフ。

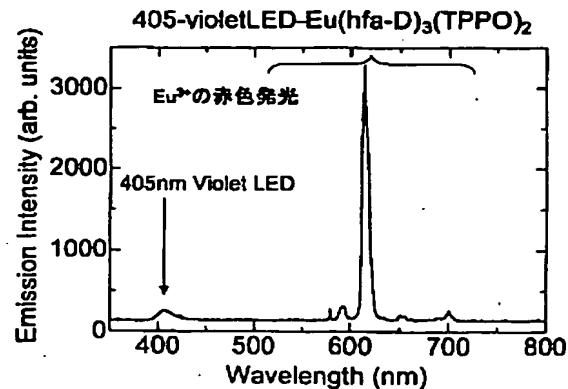
【図2】

サンプル	錯体	ポリマー	添加剤	発光量子効率 (%)	発光寿命 (ns)
A	Eu(hfa-D) <sub>3</sub> (TPPO) <sub>2</sub>	PMMA	なし	71	0.75
B	Eu(hfa-D) <sub>3</sub> (TPPO) <sub>2</sub>	PMMA	DMSO-d <sub>6</sub>	70	0.88
C	Eu(hfa-D) <sub>3</sub> (D2O) <sub>2</sub>	PMMA	なし	20	0.63
D	Eu(hfa-D) <sub>3</sub> (D2O) <sub>2</sub>	PMMA	DMSO-d <sub>6</sub>	44	0.91

【図4】

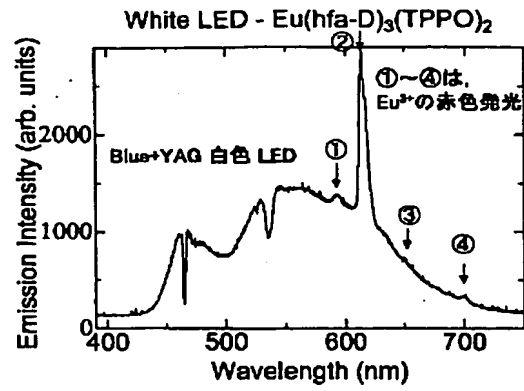


【図6】



(7)

【図7】



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(72) 発明者 島田 順一  
京都府京都市山科区小山中の川町31-3  
(72) 発明者 川上 養一  
滋賀県草津市下笠町665-6

(72) 発明者 藤田 茂夫  
京都府京都市伏見区桃山町島津47-35  
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(71)Applicant : KANSAI TLO KK

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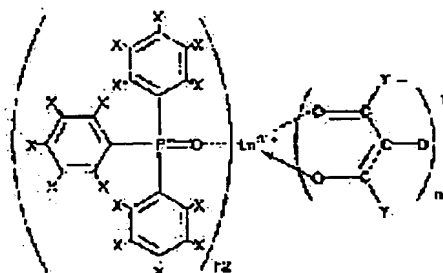
(72)Inventor : HASEGAWA SEIYA  
YANAGIDA SHOZO  
WADA YUJI  
SHIMADA JUNICHI  
KAWAKAMI YOICHI  
FUJITA SHIGEO

(54) RARE EARTH COMPLEX, OPTICALLY FUNCTIONAL MATERIAL USING THE SAME AND EMISSION DEVICE

(57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a rare earth complex and a transparent solid carrier containing the same having high phototransformation efficiency, useful as a novel emission device by being combined with an LED (light-emitting diode) or a semiconductor laser and applicable to general lighting systems, signaling devices, or displays.

**SOLUTION:** This rare earth complex for optically functional materials is expressed by general formula (I) [wherein Ln expresses a rare earth atom; n1 expresses 2 or 3; n2 expresses 1 or 2; n3 expresses 1, 2, 3 or 4; X expresses H, D, a halogen (F, Cl, Br or I), a 1-20C group, OH, nitro, amino, sulfonyl, cyano, silyl, a phosphonic acid group, diazo or mercapto; Y expresses a 1-20C group, OH, nitro, amino, sulfonyl, cyano, silyl, a phosphonic acid group, diazo or mercapto; D expresses deuterium]. This optically functional material is obtained by bringing the rare earth complex to be included in the transparent solid carrier. This emission device is provided by combining the optically functional material with the LED or the semiconductor laser.



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## \* NOTICES \*

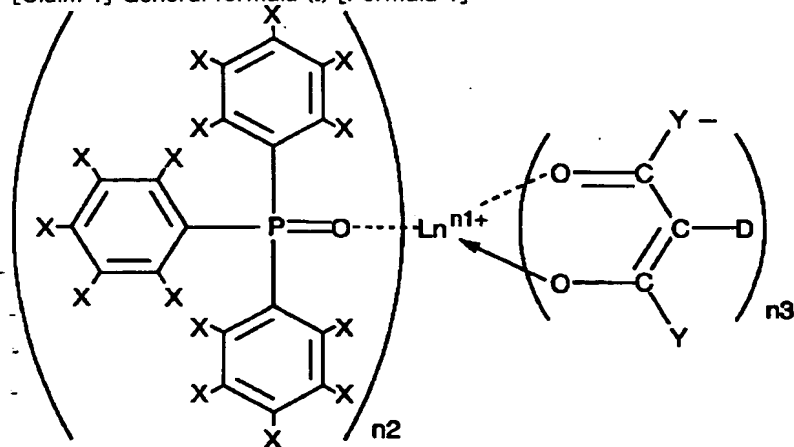
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## CLAIMS

[Claim(s)]

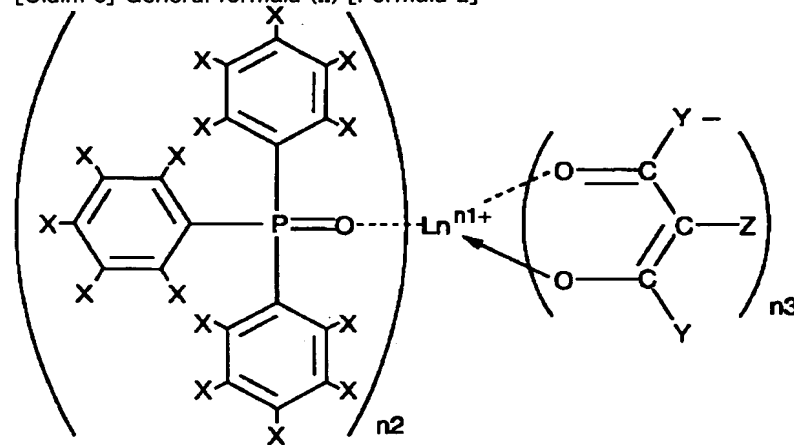
[Claim 1] General formula (I) [Formula 1]



$\text{Ln}$  shows a rare earth atom among [type, and  $n_1$  shows 2 or 3.  $n_2$  shows 1 or 2.  $n_3$  shows 1, 2, 3, or 4.  $X$  shows the same or a different hydrogen atom, a heavy hydrogen atom, a halogen atom, the radical of  $\text{C1-C20}$ , a hydroxyl group, a nitro group, the amino group, a sulfonyl group, a cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulfhydryl group.  $Y$  shows the same or a different radical of  $\text{C1-C20}$ , a hydroxyl group, a nitro group, the amino group, a sulfonyl group cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulfhydryl group.  $D$  shows a heavy hydrogen atom.] The rare earth complex for optical functional materials come out of and expressed.

[Claim 2] Transparence fixed support for optical functional materials containing a rare earth complex according to claim 1.

[Claim 3] General formula (II) [Formula 2]



[—  $\text{Ln}$ ,  $n_1$ ,  $n_2$ ,  $n_3$ ,  $X$ , and  $Y$  are the same as the above among a formula, and  $Z$  shows a hydrogen atom or a heavy hydrogen atom.] Luminescence equipment characterized by combining the light emitting diode or the semiconductor laser which emits the excitation light corresponding to absorption of the ligand of the transparence fixed support which comes out and contains the crystal of a rare earth complex or this rare earth complex expressed, and a  $f-f$  transition of central ion  $\text{Ln}^{n_1+}$  of this complex or this complex.

[Claim 4] Luminescence equipment according to claim 3 characterized by above-mentioned central ion  $\text{Ln}^{n_1+}$  being  $\text{Eu}^{3+}$ .

[Translation done.]

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the rare earth complex equipped with the useful optical property, the optical functional material which applied it to the list, and luminescence equipment.

[0002]

[Description of the Prior Art] Development of an electronic ingredient is remarkable and much development of an optical functional material is performed in the field of optoelectronics. For example, the glass containing neodymium is put in practical use as an electron device for laser beams. However, the manufacture and processing are difficult, and since the manufacturing cost is high, the application is restricted.

[0003] The resin constituent containing the ammonium salt of beta-diketone / Eu complex which has a thiophene and CF<sub>3</sub> as a substituent as a polymer constituent which has a luminescence is indicated by JP,64-26583,A. Furthermore, the resin constituent containing the deuteration beta-diketone / Eu complex, or the sulfonate / Eu complex which has a luminescence and which has CF<sub>3</sub> as a substituent as a polymer constituent is indicated by Japanese Patent Application No. 10-238973.

[0004]

[Problem(s) to be Solved by the Invention] However, these resin constituent had not reached the level which a luminescence property can still satisfy.

[0005] beginning some these artificers from re-evaluation of the energy gap theory to it — a group of rare earth metals, such as neodymium which can emit light in an organic medium for the first time in the world in 1995, — it succeeded in the design of a complex (the Hasegawa \*\*\*\*, "how the neodium which does not shine in an organic medium to be shone", chemistry, industry, volume [ 53rd ] (2000) No. 2, and pp.126-130). Patent application was also performed about these parts (PCT/JP98/00970=WO98/40388 official report, a Japanese-Patent-Application-No. 10-238973= JP,2000-63682,A official report, Japanese-Patent-Application-No. 11-62298= JP,2000-256251,A official report).

[0006] These complexes are stable also in the elevated temperature of 350 degrees C, it is hard to produce photodegradation, and an organic compound reverses the conventional common sense of being easy to produce degradation by heat or optical exposure. Moreover, compatibility with the host ingredient of a resin system called plastics and a polymer is also high, and becoming easy workability with a next-generation light corpuscle child conjointly is expected.

[0007] Then, invention-in-this-application persons did patent application of the luminescence equipment which combined the constituent which has these outstanding luminescence properties and them and LED, or semiconductor laser (application for patent No. 135116 [ 2001 to ]).

[0008] While continuing research further about a complex, extinction and a luminescence property come to find out the further excellent constituent, and this invention persons offer the constituent itself and the optical functional material using it, and luminescence equipment according to combination with it, LED, or semiconductor laser further this time.

[0009]

[Means for Solving the Problem] The constituent concerning this invention is a rare earth complex expressed with the general formula (II) of drawing 1.

[0010] In the general formula (II) of drawing 1, Ln shows a rare earth atom and n1 shows 2 or 3. n2 shows 1 or 2. n3 shows 1, 2, 3, or 4. X shows the same or a different hydrogen atom, a heavy hydrogen atom, a halogen atom (F, Cl, Br, I), the radical of C1-C20, a hydroxyl group, a nitro group, the amino group, a sulfonyl group, a cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulfhydryl group. Y shows the same or a different radical of C1-C20, a hydroxyl group, a nitro group, the amino group, a sulfonyl group cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulfhydryl group. Z shows a hydrogen atom or a heavy hydrogen atom.

[0011]

[Embodiment of the Invention] Each component is further explained to a detail.

[0012] As the radical of C1-C20;

\* Par alkyl halide radical which has a straight chain or branching, such as an alkyl group (CnH2n+1;n=1-20) which has a straight chain or branching and a perfluoroalkyl radical (CnF2n+1;n=1-20), and the Park Rollo alkyl group (CnCl2n+1;n=1-20);

[0013] \* The alkenyl radical which has a straight chain or branching (a vinyl group, an allyl group, butenyl group), and a perfluoro alkenyl radical (a perfluoro vinyl group and a perfluoro allyl group —) The par halogenation alkenyl radical which has a straight chain or branching, such as a perfluoro butenyl group and a par chloro alkenyl radical; A cycloalkyl radical (CnH2n-1;n=3-20), And a perfluoro cycloalkyl radical (CnF2n-1;n=3-20), par alkyl halide radical; which has a straight chain or branching, such as the Park Rollo alkyl group (CnCl2n-1;n=3-20), — a cyclo alkenyl radical (a cyclopentyl group —) Par alkyl halide radicals, such as perfluoro cyclo alkenyl radicals, such as a cyclohexyl radical, and a par chloro alkenyl radical;

[0014] \* Par halogenated-aromatics radicals, such as aromatic series radicals, such as a phenyl group, a naphthyl group, and a biphenyl radical, and a perfluoro phenyl group, a perfluoro naphthyl group, a perfluoro biphenyl radical, a par chlorophenyl radical, the Park Rollo naphthyl group, and a par chloro biphenyl radical;

[0015] \* Par halogenation hetero aromatic series radicals, such as hetero aromatic series radicals, such as a pyridyl radical, and a perfluoro pyridyl radical;

[0016] \* Par halogenation aralkyl radicals, such as aralkyl radicals, such as benzyl and a phenethyl radical, and perfluoro benzyl;

[0017] \*\* can be mentioned. \_\_\_\_\_

[0018] You may permute by the radical of C1-C20 shown by X and Y if needed by substituents, such as a heavy hydrogen atom, a halogen atom (F, Cl, Br, I), a hydroxyl group, a nitro group, the amino group, a sulfonyl group, a cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulfhydryl group.

[0019] Moreover, one or more -O-, -COO-, and -CO- are made to intervene between the C-C single bond of the location of the arbitration of the radical of C1-C20, and it is good also as the ether, ester, and ketone structure.

[0020] the rare earth complex of the general formula (II) X and whose Y are alkenyl radicals — the need — responding — olefins, such as ethylene and a propylene, — and halogenation olefin polymerization is carried out and it is good also as a macromolecule rare earth complex.

[0021] In the compound expressed with a general formula (II), although the aforementioned thing is usable, when the point of the stability of the transparence solid support which contains a rare earth complex or a rare earth complex especially, and luminescence reinforcement is taken into consideration as Y, the alkyl group of carbon numbers 1-4, a par alkyl halide radical, an aromatic series radical, a par halogenated-aromatics radical, a hetero aromatic series radical, and a par halogenation hetero aromatic series radical are desirable, and a perfluoroalkyl radical, an aromatic series radical, and a hetero aromatic series radical are the most desirable especially.

[0022] As rare earth elements expressed with Ln, lanthanides, such as La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, are mentioned, and Nd, Eu, Tb, and Yb are mentioned preferably.

[0023] Although n1 is 2 or 3, 3 is shown preferably. Although n2 is 1 or 2, 2 is shown preferably. Although n3 is either 1-4, 3 is shown preferably.

[0024] By carrying out the heavy hydrogen substitution reaction of the complex and deuteration agent which are expressed with a general formula (II), the complex (that whose Z is the heavy hydrogen atom D) of the general formula (I) indicated to claim 1 is obtained. Deuteration alcohol, such as heavy water, a deuteration methanol, and deuteration ethanol, a heavy hydrogen chloride, deuteration alkali, etc. are mentioned to the protonic compound and concrete target in which the deuteration agent used contains heavy hydrogen. In order to promote a reaction, base agents and additives, such as a trimethylamine and triethylamine, may be added. Although a heavy hydrogen substitution reaction is obtained by mixing the complex and deuteration agent which are expressed with a general formula (II), an aprotic solvent may be added to reaction time. As an aprotic solvent, halogen system solvents, such as ether system solvents, such as ketone solvent, such as an acetone and a methyl ethyl ketone, diethylether, and a tetrahydrofuran, chloroform, and a methylene chloride, DMSO, DMF, etc. are mentioned. inside — a general formula (II) — the dissolution — a meltable solvent is desirable.

[0025] Moreover, as an amount of the deuteration agent to be used, 1 - 100 weight section extent is illustrated to the total amount (it considers as 1 weight section) of the complex expressed with a general formula (II), and it is 1 - 20 weight section extent preferably.

[0026] What is necessary is not to be limited especially as an approach of mixing, but to be 150 degrees C in temperature from a room temperature, to be 30 to 100 degrees C in temperature preferably, and just to mix preferably under churning for 0.1 to 20 hours for 0.1 to 100 hours if needed.

[0027] The complex expressed with a general formula (I) is obtained by distilling off a deuteration agent and a solvent after churning. Moreover, it can refine further by approaches, such as recrystallization, column chromatography, and sublimation, if needed.

[0028] They are a general formula (I) and a general formula (II) by the above-mentioned approach. The rare earth complex expressed can be prepared.

[0029] The extinction and the luminescence property of the rare earth complex concerning this invention are described in detail later.

[0030] the above — it can use for various optical functional materials, such as a luminescence auxiliary object and an optical lens, by making a transparence solid support contain the rare earth complex which has useful extinction and luminescence property. In addition, the crystal of the above-mentioned rare earth complex itself can be used as an optical functional material similarly natural.

[0031] Furthermore, the luminescence equipment which combined the light emitting diode or the semiconductor laser which emits the excitation light corresponding to f-f transition of the central ion of the transparence solid support containing the crystal of these rare earth complex or a rare earth complex and its rare earth complex or absorption of a ligand can be used as high luminescence equipment of luminous efficiency.

[0032] A transparence polymer matrix, clear glass, etc. can be used as the above-mentioned transparence solid support.

[0033] As a transparence polymer matrix, polymethylmethacrylate, fluorine-containing polymethacrylate, Polyacrylate, fluorine-containing polyacrylate, polystyrene, polyethylene, Polyolefines, such as polypropylene and polybutene, fluorine-containing polyolefine, Polyvinyl ether, fluorine-containing polyvinyl ether, polyvinyl acetate, Polyvinyl chlorides and those copolymers, a cellulose, polyacetal, Polyester, a polycarbonate, an epoxy resin, polyamide resin, Polyimide resin, polyurethane, Nafion, petroleum resin, rosin, silicone resin, etc. are illustrated. Polymethylmethacrylate, fluorine-containing polymethacrylate, polyacrylate, fluorine-containing polyacrylate, polystyrene, polyolefine, polyvinyl ether and those copolymers, an epoxy resin, etc. can be used preferably. Of course, these two or more sorts may be combined.

[0034] When making a transparence polymer matrix, clear glass, etc. contain a rare earth complex, in order to raise the transparency, a polar solvent can also be included simultaneously.

[0035] As a polar solvent, DMSO-d6 (dimethyl sulfoxide) can be used, for example.

[0036]

[Effect of the Invention] The transparence solid support containing the rare earth complex of this invention and it has the high conversion efficiency of light, it is useful as new luminescence equipment by combination with LED or semiconductor laser, and the application to general lighting equipment, a signalling device, a display, etc. is possible for it.

[0037] By changing the structure of a ligand, and/or the class of rare earth atom, the rare earth complex of this invention can change luminescence wavelength, and can obtain coloring of the wavelength of arbitration.

[0038]

[Example] Although this invention is hereafter explained more to a detail based on an example, as for this invention itself, it is needless to say that it is not limited by these examples.

[0039] The synthetic acetic acid europium ( $\text{Eu}(\text{CH}_3\text{COO})_3 \cdot 5\text{H}_2\text{O}$ ) 3:5g, 12.5mmol) of  $\text{Eu}(\text{hfa}-\text{H})_3(\text{H}_2\text{O})_2$  complex was melted to 50ml distilled water, the hexafluoro acetylacetone (hfa) ( $\text{CF}_3\text{COCH}_2\text{COCF}_3$ : 7g, 33.6mmol) was added, and it agitated at the room temperature for 3 hours. The precipitating solid-state was recrystallized with after filtration and rinsing, a methanol, and distilled water, and the target complex ( $\text{Eu}(\text{hfa}-\text{H})_3(\text{H}_2\text{O})_2$ : light yellow) was obtained. By differential thermal analysis (DSC), the obtained complex checked that they were two hydrates. IR ( $\text{cm}^{-1}$ ): 3450 (O-H st.), 1650 (C=O st.), 1250-1150 (C-F) 19 F-NMR:(acetone -  $\text{d}_6$ , standard substance  $\text{C}_6\text{F}_6$ ; ppm)-78.3 [( $\text{CF}_3$ )0040] The complex ( $\text{Eu}(\text{hfa}-\text{H})_3(\text{H}_2\text{O})_2$  5.77g) and triphenyl phosphine oxide (TPPO:2.97g) which were obtained in the synthetic example 1 of  $\text{Eu}(\text{hfa}-\text{H})_3(\text{TPPO})_2$  complex were melted to the 100ml methanol, and heating reflux was performed for 12 hours. The methanol was removed by reduced pressure distilling off 12 hours after, and the white product was obtained. After washing these fine particles with toluene and removing  $\text{Eu}(\text{hfa}-\text{H})_3(\text{H}_2\text{O})_2$  unreacted complex by attraction filtration, reduced pressure distilling off of the toluene was carried out. The obtained product was washed by the hexane and fine particles were obtained. Yield was 5.28g and yield was 74%. The target complex ( $\text{Eu}(\text{hfa}-\text{H})_3(\text{TPPO})_2$ ) was obtained by recrystallizing with the mixed solvent of toluene and a hexane.

IR ( $\text{cm}^{-1}$ ): 1650 (C=O) 1250-1150 (C-F), 1125 (P=O) 19 F-NMR : (acetone -  $\text{d}_6$ , standard substance  $\text{C}_6\text{F}_6$ ; ppm) delta-76.7 1 (s, C-F) H-NMR (acetone -  $\text{d}_6$ , standard substance TMS; ppm) : delta 7.6 (m, aromatic C-H), 5.4 (s, C-H) Elemental analysis ( $\text{EuC}_{51}\text{H}_{33}\text{O}_{8}\text{F}_{18}\text{P}_2$ )

Actual measurement C, 45.94;H, 2.57% calculated value C, 45.96;H, 2.50% [0041] The deuteration reaction of the complex obtained in the synthetic example 2 of  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$  was performed according to well-known reference (Hasegawa, Y.; Murakoshi, K.; Wada, Y.; Yanagida, S.; Kim, J.; Nakashima, N.; Yamanaka, T.J.Phys.Chem.1996, 100, 10201.). The obtained fine particles were fully dried and the target complex ( $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$ ) was obtained.

[0042] The polymer containing the complex obtained in the creation example 3 of the polymer containing  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$  prepared according to well-known reference (Hasegawa, Y.; Sogabe, K.; Wada, Y.; Kitamura, T.; Nakashima, N.; Yanagida, S.Chem.Lett.1999, 35.).

[0043] The luminescence property of the PMMA polymer (A, B) containing luminescence property  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$  is shown in drawing 2. The luminescence property of the PMMA polymer (Hasegawa, Y.; Sogabe, K.; Wada, Y.; Kitamura, T.; Nakashima, N.; Yanagida, S.Chem.Lett.1999, 35.) (C, D) which contains a rare earth complex given in reference as a comparison is shown in the same graph. Drawing 2 shows that the luminescence quantum yield of the transparency solid support (A, B) containing the complex of this invention is improving by leaps and bounds compared with a thing (PMMA containing  $\text{Eu}(\text{hfa}-\text{D})_3(\text{D}_2\text{O})_2$ ) (C, D) given in reference.

[0044] The graph of the emission spectrum of each sample is shown in drawing 3. The spectral intensity of an axis of ordinate standardized the luminescence reinforcement of 590nm as 1. Excitation wavelength is 465nm corresponding to f-f transition of  $\text{Eu}^{3+}$  which is the central ion of a complex. As for the sample A (PMMA containing  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$ ) which is the example of this invention, it turns out that the luminescence reinforcement of 615nm (red) is strong relatively. Moreover, in drawing 3, it is observed that the peak intensity ratios of each sample differ. This shows that the color rendering properties of luminescence can be adjusted in a certain range by designing selection of a ligand, and the existence (amount) of an additive suitably.

[0045] The excitation spectrum of the sample A (PMMA containing  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$ ) which is the example of this invention is shown in drawing 4. It has a broadcloth absorption band besides a 465nm sharp peak in 370-450nm. It is thought that 465nm is based on f-f transition of central ion  $\text{Eu}^{3+}$  as above-mentioned, and a 370-450nm broadcloth absorption band is based on the thing which many f-f transition overlapped, or a ligand.

[0046] Drawing 5 puts Sample A (PMMA containing  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$ ) on InGaN blue LED, and measures the spectrum of the transmitted light. Although InGaN-LED adjusts the component variable x so that the core of the luminescence wavelength may be set to 465nm, and it has a luminescence peak in 450-500nm, in 465nm, the steep absorption peak by f-f transition of central ion  $\text{Eu}^{3+}$  of rare earth complex  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$  has arisen in it. Moreover, the big luminescence peak has appeared in 615nm, and the small luminescence peak has appeared also near 591nm and in near 700nm. The high luminous efficiency of about 70% in these is acquired as shown in drawing 2.

[0047] Drawing 6 is the result of adjusting the component variable x of InGaN-LED so that it may go into the 370-450nm broadcloth excitation Mitsunori enclosure of Sample A (PMMA containing  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$ ), and performing measurement same as 405nm for luminescence wavelength. Also in this case, similarly, the big peak appeared near 615nm and the small peak has appeared 591nm and near 700nm.

[0048] Drawing 7 is the result of putting Sample A (PMMA containing  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$ ), and performing same measurement on the conventional white LED (what covered InGaN blue LED with the YAG fluorescent substance). In 465nm, the absorption peak by f-f transition of  $\text{Eu}^{3+}$  is accepted clearly. And the big luminescence peak has appeared near 615nm as the result. It will become near white and the ideal light source using it for which the red component which was missing in the conventional white LED was compensated with the luminescence equipment produced by doing in this way will turn into a source of the white light where color rendering properties are dramatically high so that clearly from this drawing. An operation, a goods display, etc. can use especially this as the useful light source in the field for which the color discernment force or color rendering properties is needed.

[0049] Since the rare earth complex concerning this invention has such an extinction property, it can be used useful as an efficient wavelength conversion light functional material by combining LED or semiconductor laser as the excitation light source. It is thought that especially a 370-450nm broadcloth absorption band as shown in drawing 4 brings big effectiveness to combination with broadband emitters, such as EL.

[0050] The usefulness of such a wavelength conversion light functional material and it and LED, or the luminescence equipment by combination with semiconductor laser is discussed in the detail in application (application for patent 2001-135116) of the above-mentioned point. The optical functional material which is a transparency solid support containing the rare earth complex and it concerning this invention, and luminescence equipment according to combination with the emitter of it, LED, semiconductor laser, and others further provide society with the same industrial usefulness.

[Translation done.]

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**TECHNICAL FIELD**

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[Field of the Invention] This invention relates to the rare earth complex equipped with the useful optical property, the optical functional material which applied it to the list, and luminescence equipment.

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**PRIOR ART**

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[Description of the Prior Art] Development of an electronic ingredient is remarkable and much development of an optical functional material is performed in the field of optoelectronics. For example, the glass containing neodymium is put in practical use as an electron device for laser beams. However, the manufacture and processing are difficult, and since the manufacturing cost is high, the application is restricted.

[0003] The resin constituent containing the ammonium salt of beta-diketone / Eu complex which has a thiophene and CF<sub>3</sub> as a substituent as a polymer constituent which has a luminescence is indicated by JP,64-26583,A. Furthermore, the resin constituent containing the deuteration beta-diketone / Eu complex, or the sulfonate / Eu complex which has a luminescence and which has CF<sub>3</sub> as a substituent as a polymer constituent is indicated by Japanese Patent Application No. 10-238973.

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EFFECT OF THE INVENTION

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[Effect of the Invention] The transparence solid support containing the rare earth complex of this invention and it has the high conversion efficiency of light, it is useful as new luminescence equipment by combination with LED or semiconductor laser, and the application to general lighting equipment, a signalling device, a display, etc. is possible for it.

[0037] By changing the structure of a ligand, and/or the class of rare earth atom, the rare earth complex of this invention can change luminescence wavelength, and can obtain coloring of the wavelength of arbitration.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] However, these resin constituent had not reached the level which a luminescence property can still satisfy.

[0005] beginning some these artificers from re-evaluation of the energy gap theory to it — a group of rare earth metals, such as neodymium which can emit light in an organic medium for the first time in the world in 1995, — it succeeded in the design of a complex (the Hasegawa \*\*\*\*, "how the neodium which does not shine in an organic medium to be shone", chemistry, industry, volume [ 53rd ] (2000) No. 2, and pp.126-130). Patent application was also performed about these parts (PCT/JP98/00970=WO98/40388 official report, a Japanese-Patent-Application-No. 10-238973= JP,2000-63682,A official report, Japanese-Patent-Application-No. 11-62298= JP,2000-256251,A official report).

[0006] These complexes are stable also in the elevated temperature of 350 degrees C, it is hard to produce photodegradation, and an organic compound reverses the conventional common sense of being easy to produce degradation by heat or optical exposure. Moreover, compatibility with the host ingredient of a resin system called plastics and a polymer is also high, and becoming easy workability with a next-generation light corpuscle child conjointly is expected.

[0007] Then, invention-in-this-application persons did patent application of the luminescence equipment which combined the constituent which has these outstanding luminescence properties and them and LED, or semiconductor laser (application for patent No. 135116 [ 2001 to ]).

[0008] While continuing research further about a complex, extinction and a luminescence property come to find out the further excellent constituent, and this invention persons offer the constituent itself and the optical functional material using it, and luminescence equipment according to combination with it, LED, or semiconductor laser further this time.

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## MEANS

[Means for Solving the Problem] The constituent concerning this invention is a rare earth complex expressed with the general formula (II) of drawing 1.

[0010] In the general formula (II) of drawing 1, Ln shows a rare earth atom and n1 shows 2 or 3. n2 shows 1 or 2. n3 shows 1, 2, 3, or 4. X shows the same or a different hydrogen atom, a heavy hydrogen atom, a halogen atom (F, Cl, Br, I), the radical of C1-C20, a hydroxyl group, a nitro group, the amino group, a sulfonyl group, a cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulfhydryl group. Y shows the same or a different radical of C1-C20, a hydroxyl group, a nitro group, the amino group, a sulfonyl group, a cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulfhydryl group. Z shows a hydrogen atom or a heavy hydrogen atom.

[0011]

[Embodiment of the Invention] Each component is further explained to a detail.

[0012] As the radical of C1-C20;

\* Par alkyl halide radical which has a straight chain or branching, such as an alkyl group ( $C_nH_{2n+1}$ ;  $n=1-20$ ) which has a straight chain or branching and a perfluoroalkyl radical ( $C_nF_{2n+1}$ ;  $n=1-20$ ), and the Park Rollo alkyl group ( $C_nCl_{2n+1}$ ;  $n=1-20$ );

[0013] \* The alkenyl radical which has a straight chain or branching (a vinyl group, an allyl group, butenyl group), and a perfluoro alkenyl radical (a perfluoro vinyl group and a perfluoro allyl group —) The par halogenation alkenyl radical which has a straight chain or branching, such as a perfluoro butenyl group and a par chloro alkenyl radical; A cycloalkyl radical ( $C_nH_{2n-1}$ ;  $n=3-20$ ), And a perfluoro cycloalkyl radical ( $C_nF_{2n-1}$ ;  $n=3-20$ ), par alkyl halide radical; which has a straight chain or branching, such as the Park Rollo alkyl group ( $C_nCl_{2n-1}$ ;  $n=3-20$ ), — a cyclo alkenyl radical (a cyclopentyl group —) Par alkyl halide radicals, such as perfluoro cyclo alkenyl radicals, such as a cyclohexyl radical, and a par chloro alkenyl radical;

[0014] \* Par halogenated-aromatics radicals, such as aromatic series radicals, such as a phenyl group, a naphthyl group, and a biphenyl radical, and a perfluoro phenyl group, a perfluoro naphthyl group, a perfluoro biphenyl radical, a par chlorophenyl radical, the Park Rollo naphthyl group, and a par chloro biphenyl radical;

[0015] \* Par halogenation hetero aromatic series radicals, such as hetero aromatic series radicals, such as a pyridyl radical, and a perfluoro pyridyl radical;

[0016] \* Par halogenation aralkyl radicals, such as aralkyl radicals, such as benzyl and a phenethyl radical, and perfluoro benzyl;

[0017] \*\* can be mentioned.

[0018] You may permute by the radical of C1-C20 shown by X and Y if needed by substituents, such as a heavy hydrogen atom, a halogen atom (F, Cl, Br, I), a hydroxyl group, a nitro group, the amino group, a sulfonyl group, a cyano group, a silyl radical, a phosphonic acid radical, a diazo group, and a sulfhydryl group.

[0019] Moreover, one or more -O-, -COO-, and -CO- are made to intervene between the C-C single bond of the location of the arbitration of the radical of C1-C20, and it is good also as the ether, ester, and ketone structure.

[0020] the rare earth complex of the general formula (II) X and whose Y are alkenyl radicals — the need — responding — olefins, such as ethylene and a propylene, — and halogenation olefin polymerization is carried out and it is good also as a macromolecule rare earth complex.

[0021] In the compound expressed with a general formula (II), although the aforementioned thing is usable, when the point of the stability of the transparence solid support which contains a rare earth complex or a rare earth complex especially, and luminescence reinforcement is taken into consideration as Y, the alkyl group of carbon numbers 1-4, a par alkyl halide radical, an aromatic series radical, a par halogenated-aromatics radical, a hetero aromatic series radical, and a par halogenation hetero aromatic series radical are desirable, and a perfluoroalkyl radical, an aromatic series radical, and a hetero aromatic series radical are the most desirable especially.

[0022] As rare earth elements expressed with Ln, lanthanides, such as La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, are mentioned, and Nd, Eu, Tb, and Yb are mentioned preferably.

[0023] Although n1 is 2 or 3, 3 is shown preferably. Although n2 is 1 or 2, 2 is shown preferably. Although n3 is either 1-4, 3 is shown preferably.

[0024] By carrying out the heavy hydrogen substitution reaction of the complex and deuteration agent which are expressed with a general formula (II), the complex (that whose Z is the heavy hydrogen atom D) of the general formula (I) indicated to claim 1 is obtained. Deuteration alcohol, such as heavy water, a deuteration methanol, and deuteration ethanol, a heavy hydrogen chloride, deuteration alkali, etc. are mentioned to the protonic compound and concrete target in which the deuteration agent used contains heavy hydrogen. In order to promote a reaction, base agents and additives, such as a trimethylamine and triethylamine, may be added. Although a heavy hydrogen substitution reaction is obtained by mixing the complex and deuteration agent which are expressed with a general formula (II), an aprotic solvent may be added to reaction time. As an aprotic solvent, halogen system solvents, such as ether system solvents, such as ketone solvent, such as an acetone and a methyl ethyl ketone, diethylether, and a tetrahydrofuran, chloroform, and a methylene chloride, DMSO, DMF, etc. are mentioned. inside — a general formula (II) — the dissolution — a meltable solvent is desirable.

[0025] Moreover, as an amount of the deuteration agent to be used, 1 - 100 weight section extent is illustrated to the total amount (it considers as 1 weight section) of the complex expressed with a general formula (II), and it is 1 - 20 weight section extent preferably.

[0026] What is necessary is not to be limited especially as an approach of mixing, but to be 150 degrees C in

temperature from a room temperature, to be 30 to 100 degrees C in temperature preferably, and just to mix preferably under churning for 0.1 to 20 hours for 0.1 to 100 hours if needed.

[0027] The complex expressed with a general formula (I) is obtained by distilling off a deuteration agent and a solvent after churning. Moreover, it can refine further by approaches, such as recrystallization, column chromatography, and sublimation, if needed.

[0028] They are a general formula (I) and a general formula (II) by the above-mentioned approach. The rare earth complex expressed can be prepared.

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[0033] As a transparence polymer matrix, polymethylmethacrylate, fluorine-containing polymethacrylate, Polyacrylate, fluorine-containing polyacrylate, polystyrene, polyethylene, Polyolefines, such as polypropylene and polybutene, fluorine-containing polyolefine, Polyvinyl ether, fluorine-containing polyvinyl ether, polyvinyl acetate, Polyvinyl chlorides and those copolymers, a cellulose, polyacetal, Polyester, a polycarbonate, an epoxy resin, polyamide resin, Polyimide resin, polyurethane, Nafion, petroleum resin, rosin, silicone resin, etc. are illustrated. Polymethylmethacrylate, fluorine-containing polymethacrylate, polyacrylate, fluorine-containing polyacrylate, polystyrene, polyolefine, polyvinyl ether and those copolymers, an epoxy resin, etc. can be used preferably. Of course, these two or more sorts may be combined.

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## EXAMPLE

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Actual measurement C, 45.94;H, 2.57% calculated value C, 45.96;H, 2.50% [0041] The deuteration reaction of the complex obtained in the synthetic example 2 of  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$  was performed according to well-known reference (Hasegawa, Y.; Murakoshi, K.; Wada, Y.; Yanagida, S.; Kim, J.; Nakashima, N.; Yamanaka, T.J.Phys.Chem.1996, 100, 10201.). The obtained fine particles were fully dried and the target complex ( $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$ ) was obtained.

[0042] The polymer containing the complex obtained in the creation example 3 of the polymer containing  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$  prepared according to well-known reference (Hasegawa, Y.; Sogabe, K.; Wada, Y.; Kitamura, T.; Nakashima, N.; Yanagida, S.Chem.Lett.1999, 35.).

[0043] The luminescence property of the PMMA polymer (A, B) containing luminescence property  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$  is shown in drawing 2. The luminescence property of the PMMA polymer (Hasegawa, Y.; Sogabe, K.; Wada, Y.; Kitamura, T.; Nakashima, N.; Yanagida, S.Chem.Lett.1999, 35.) (C, D) which contains a rare earth complex given in reference as a comparison is shown in the same graph. Drawing 2 shows that the luminescence quantum yield of the transparency solid support (A, B) containing the complex of this invention is improving by leaps and bounds compared with a thing (PMMA containing  $\text{Eu}(\text{hfa}-\text{D})_3(\text{D}_2\text{O})_2$ ) (C, D) given in reference.

[0044] The graph of the emission spectrum of each sample is shown in drawing 3. The spectral intensity of an axis of ordinate standardized the luminescence reinforcement of 590nm as 1. Excitation wavelength is 465nm corresponding to f-f transition of  $\text{Eu}^{3+}$  which is the central ion of a complex. As for the sample A (PMMA containing  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$ ) which is the example of this invention, it turns out that the luminescence reinforcement of 615nm (red) is strong relatively. Moreover, in drawing 3, it is observed that the peak intensity ratios of each sample differ. This shows that the color rendering properties of luminescence can be adjusted in a certain range by designing selection of a ligand, and the existence (amount) of an additive suitably.

[0045] The excitation spectrum of the sample A (PMMA containing  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$ ) which is the example of this invention is shown in drawing 4. It has a broadcloth absorption band besides a 465nm sharp peak in 370-450nm. It is thought that 465nm is based on f-f transition of central ion  $\text{Eu}^{3+}$  as above-mentioned, and a 370-450nm broadcloth absorption band is based on the thing which many f-f transition overlapped, or a ligand.

[0046] Drawing 5 puts Sample A (PMMA containing  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$ ) on InGaN blue LED, and measures the spectrum of the transmitted light. Although InGaN-LED adjusts the component variable x so that the core of the luminescence wavelength may be set to 465nm, and it has a luminescence peak in 450-500nm, in 465nm, the steep absorption peak by f-f transition of central ion  $\text{Eu}^{3+}$  of rare earth complex  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$  has arisen in it. Moreover, the big luminescence peak has appeared in 615nm, and the small luminescence peak has appeared also near 591nm and in near 700nm. The high luminous efficiency of about 70% in these is acquired as shown in drawing 2.

[0047] Drawing 6 is the result of adjusting the component variable x of InGaN-LED so that it may go into the 370-450nm broadcloth excitation Mitsunori enclosure of Sample A (PMMA containing  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$ ), and performing measurement same as 405nm for luminescence wavelength. Also in this case, similarly, the big peak appeared near 615nm and the small peak has appeared 591nm and near 700nm.

[0048] Drawing 7 is the result of putting Sample A (PMMA containing  $\text{Eu}(\text{hfa}-\text{D})_3(\text{TPPO})_2$ ), and performing same measurement on the conventional white LED (what covered InGaN blue LED with the YAG fluorescent substance). In 465nm, the absorption peak by f-f transition of  $\text{Eu}^{3+}$  is accepted clearly. And the big luminescence peak has appeared near 615nm as the result. It will become near white and the ideal light source using it for which the red component which was missing in the conventional white LED was compensated with the luminescence equipment produced by doing in this way will turn into a source of the white light where color rendering properties are dramatically high so that clearly from this drawing. An operation, a goods display, etc. can use especially this as the useful light source in the field for which the color discernment force or color rendering properties is needed.

[0049] Since the rare earth complex concerning this invention has such an extinction property, it can be used useful as an efficient wavelength conversion light functional material by combining LED or semiconductor laser as the excitation

light source. It is thought that especially a 370-450nm broadcloth absorption band as shown in drawing 4 brings big effectiveness to combination with broadband emitters, such as EL.

[0050] The usefulness of such a wavelength conversion light functional material and it and LED, or the luminescence equipment by combination with semiconductor laser is discussed in the detail in application (application for patent 2001-135116) of the above-mentioned point. The optical functional material which is a transparence solid support containing the rare earth complex and it concerning this invention, and luminescence equipment according to combination with the emitter of it, LED, semiconductor laser, and others further provide society with the same industrial usefulness.

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[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The general formula of the rare earth complex concerning this invention.

[Drawing 2] The correlation table of the luminescence property of the rare earth complex which is the example of this invention, and the rare earth complex of a comparison compound.

[Drawing 3] The graph of the emission spectrum of the rare earth complex which is the example of this invention, and the rare earth complex of a comparison compound.

[Drawing 4] The graph of the excitation spectrum of the rare earth complex which is the example of this invention.

[Drawing 5] The graph of the result of having put Sample A on InGaN blue LED with a main luminescence wavelength of 465nm, and having measured the spectrum of the transmitted light.

[Drawing 6] The graph of the result of having put Sample A on InGaN purple LED with a main luminescence wavelength of 405nm, and having measured the spectrum of the transmitted light.

[Drawing 7] The graph of the result of having put Sample A on white LED which covered InGaN blue LED with the YAG fluorescent substance, and having measured the spectrum of the transmitted light.

[Translation done.]

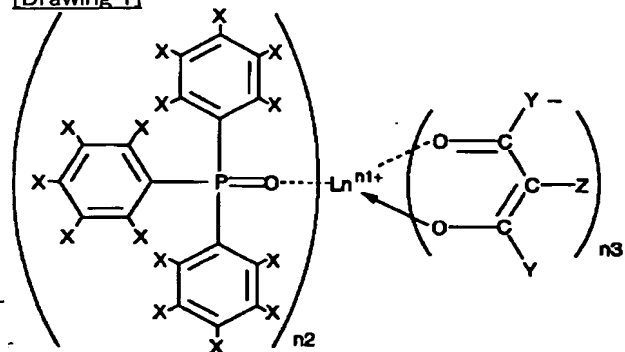
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DRAWINGS

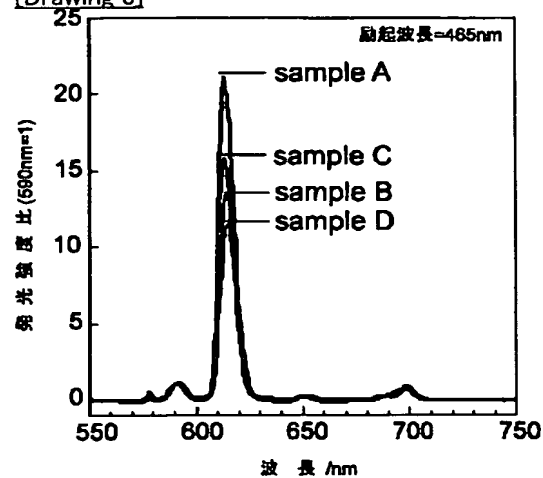
[Drawing 1]



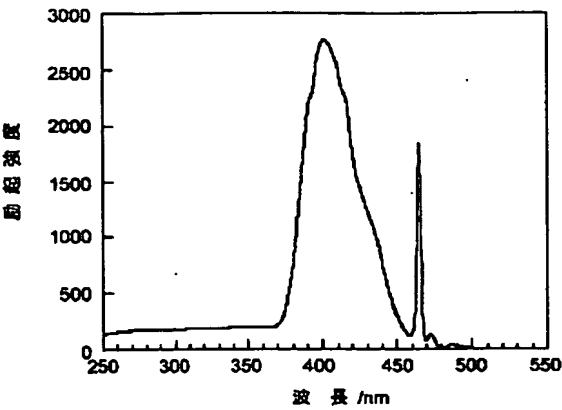
[Drawing 2]

サンプル	錯体	ポリマー	添加剤	発光量子効率 (%)	発光寿命 (ns)
A	Eu(Thfa-D) <sub>3</sub> (TPPO) <sub>2</sub>	PMMA	なし	71	0.75
B	Eu(Thfa-D) <sub>3</sub> (TPPO) <sub>2</sub>	PMMA	DMSO-d <sub>6</sub>	70	0.88
C	Eu(Thfa-D) <sub>3</sub> (D2O) <sub>2</sub>	PMMA	なし	20	0.63
D	Eu(Thfa-D) <sub>3</sub> (D2O) <sub>2</sub>	PMMA	DMSO-d <sub>6</sub>	44	0.91

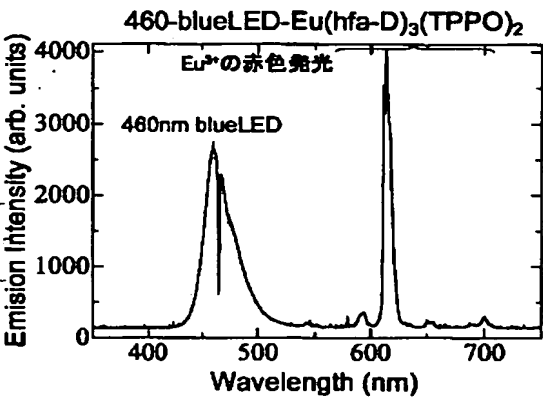
[Drawing 3]



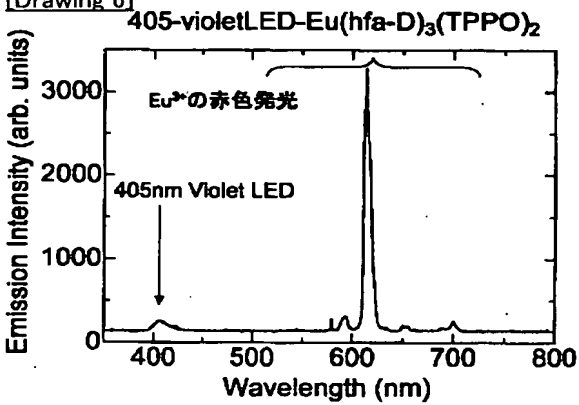
[Drawing 4]



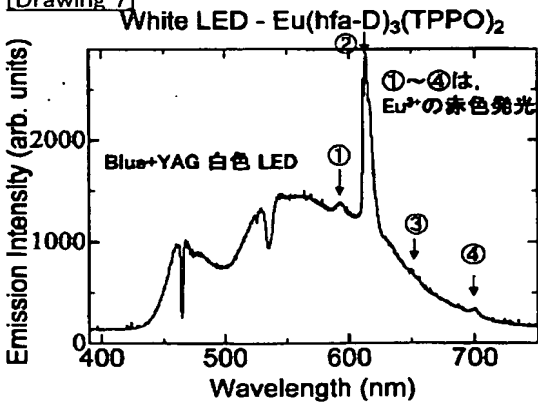
[Drawing 5]



[Drawing 6]



[Drawing 7]



[Translation done.]

